

New Low Sulfur in Diesel Fuel SRMs

Both the US and the European Union (EU) have mandated ultra-low sulfur diesel (ULSD) fuel for on-road use to make possible more efficient exhaust emission after-treatment technology which will result in substantially reduced particulate emissions from diesel engines. The EU mandated a 10 µg/g (ppm) sulfur limit in diesel starting in 2005, and the US will phase in a 15 µg/g limit beginning June 2006. The accurate determination of sulfur in ULSD at these levels is a major measurement challenge with enormous economic consequences, mostly in avoided costs, for petroleum refineries and in every link in the distribution system. Although the regulated levels are different for the EU and the US, the demands on refineries are essentially identical because in both cases the refineries will need to produce diesel fuel with a sulfur concentration near 7 µg/g to ensure that the level at the retail outlets meets the mandated specifications. To meet this challenge in a cost effective manner and with the least disruption in product availability, the industry must have highly accurate real-matrix sulfur standards. NIST has responded with the production of three distillate fuel reference materials.

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The US and the European Union (EU) have mandated ultra-low sulfur diesel (ULSD) fuel for on-road use to reduce particulate emissions from diesel engines. The new US limit is 30 times lower (15 µg/g versus 500 µg/g) than the current regulatory limit, although higher than the EU mandate of 10 µg/g. However, diesel fuel in the US is moved long distances by pipeline, which makes it more susceptible to contamination; therefore the sulfur concentration at refineries must be near 7 µg/g to ensure retail outlets meet regulatory requirements, which is essentially the same concentration level required for EU refineries. The US Environmental Protection Agency (EPA) estimates that the health and welfare benefits of this new regulation will be about \$150 billion annually to the American public. *Per capita* benefits in the EU should be similar because their consumption of diesel is slightly greater than that of the US and their population is larger.

Three distillate fuel reference materials were certified both below and above the mandated levels as shown in Table 1. Of particular interest to the industry is the zero sulfur level diesel fuel, RM 8771. These SRMs complement the four existing distillate fuel SRMs at sulfur concentrations of 11 µg/g, 427 µg/g, 1731 µg/g, and 3882 µg/g. The near-zero sulfur level diesel fuel was needed by the petroleum indus-

try for two very important reasons. First, to perform accurate measurements at the 5 µg/g to 15 µg/g level, a standard below 5 µg/g is needed. A zero-level standard is extremely helpful in determining linearity at the low end of the calibration curve. Second, this material will serve as the low-end member diluent for the preparation of intermediate standards as suggested in the forthcoming paper by Kelly et al. (2006). This material may be blended with existing diesel fuel SRMs to make calibration or check samples in the 5 µg/g to 15 µg/g range with expanded uncertainties less than 1 µg/g. The RM has already been used by EPA in a large round robin conducted in July and August of 2005.

**Table 1. List of Distillate Fuel Reference Materials
Certified in FY 2005**

SRM or RM	Name	Sulfur Content µg/g (± 95 % CI)	# of Units Sold in FY05
SRM 1616b	Sulfur in Kerosene	8.41 ± 0.12	503
SRM 2770	Sulfur in Diesel Fuel Oil	41.57 ± 0.39	147
RM 8771	Sulfur in Diesel Fuel Blend Stock	0.071 ± 0.014	246

The new fossil fuel reference standards produced this year are needed by analytical chemistry laboratories in the petroleum industry to calibrate instruments and as check samples to demonstrate quality control and regulatory compliance.

Prior to these standards, fossil fuel SRMs below 15 µg/g of sulfur had not been certified by NIST or any other National Metrology Institute. Both thermal ionization mass spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) have sufficient sensitivity at this level for a measurement of better than 1 % relative precision. At about 100 µg/g, the chemical processing blank is equal to the measurement uncertainty, and below this value it

becomes the major source of uncertainty. SRMs 1616b and 2770 were certified using our new least squares procedure that incorporates the blank and measurement uncertainty simultaneously. The same approach was used for SRM 2771/RM 8771 but because the amount of sulfur process was close to the blank amount the uncertainty was relative large. Preliminary measurements by thermal ionization mass spectrometry established that the sulfur concentration in this material was less than 0.37 $\mu\text{g/g}$ with essentially 100 % uncertainty. As expected the chemical blank was the limiting factor in the preliminary measurements.

Soon after the completion of these measurements two new analytical instruments for the determination of sulfur became available to us. These instruments are based on combustion of the sample and the ultraviolet detection of the SO_2 liberated from the sample. They are not very precise, but they have high sensitivity and were believed to have very low chemical blanks. A series of mixtures of the candidate material were mixed gravimetrically with two different diesel fuel SRMs and the mixtures were sent to two different laboratories for analysis. This procedure uses a new completely general standard additions approach based on gravimetry instead of volumetry (Kelly and Guthrie, 2006). This approach was successful and yielded a mean value of 0.071 $\mu\text{g/g}$ and a 95 % confidence level of 0.014 $\mu\text{g/g}$. This material was issued as a Reference Material (RM 8771) because not all sources of uncertainty could be evaluated (see Future Plans).

Impact: The combined impact of all NIST distillate SRMs on the ability of the petroleum industry to control diesel fuel quality in terms of sulfur content will be enormous. The three materials listed in Table 1 were used in the re-

cent EPA ULSD Round Robin consisting of 161 laboratories utilizing 208 instruments. The near-zero material will serve both as a zero-level material for calibration curves and as a diluent for mixing calibration materials in house at levels below 50 $\mu\text{g/g}$ as described in the upcoming paper by Kelly *et al.* (2006). Laboratories employing this procedure will be able to mix RM 8771 with existing diesel fuel SRMs and prepare calibration standards at any level between 5 $\mu\text{g/g}$ and 20 $\mu\text{g/g}$ with combined uncertainties less than 1 $\mu\text{g/g}$. This will make possible the implementation of the new EPA regulations.

Future Plans: The immediate future plan is to certify RM 8771 as SRM 2771. Preliminary measurements by intermediate resolution ICP-MS indicate that this technique can produce accurate concentration measurements that will make certification possible in FY2006. In addition, the plan is to re-certify SRM 2723a with a much lower uncertainty using a new double spike technique (Mann and Kelly, 2005)

Publications:

Kelly, WR, MacDonald, BS, and Leigh, SD (2006) *“Determination of Sulfur in Fossil Fuels: User Prepared Standards with Concentrations and Uncertainties Traceable to NIST Values,”* to be submitted to Journal of ASTM International.

Kelly, WR and Guthrie, WF (2006) *“A General Approach to the Standard Addition Method in Instrumental Analysis,”* to be submitted to Analytical Chemistry.

Mann, JL and Kelly, WR (2005) *“Measurement of sulfur isotope composition ($\delta^{34}\text{S}$) by multiple-collector thermal ionization mass spectrometry using a ^{33}S - ^{36}S double spike,”* Rapid Commun. Mass Spectrom. **19**, 3429-3441.